Field emission theory of dislocation-sensitized photo-stimulated exo-electron emission from coloured alkali halide crystals

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Abstract. A new field emission theory of dislocation-sensitized photo-stimulated exo-electron emission (DSPEE) is proposed, which shows that the increase in the intensity of photo emission from F-centres during plastic deformation is caused by the appearance of an electric field which draws excited electrons out of the deeper layer and, therefore, increases the number of electrons which reach the surface. The theory of DSPEE shows that the variation of DSPEE flux intensity should obey the following relation

$$\frac{\Delta J_e(\varepsilon)}{J_e(o)} = \left[\frac{Y_S}{d_F} \exp\left(\frac{\chi}{kT}\right) - 1 \right].$$

The theory of DSPEE is able to explain several experimental observations like linear increase of DSPEE intensity J_e with the strain at low deformation, occurrence of the saturation in J_e at higher deformation, temperature dependence of J_e, linear dependence of J_e on the electric field strength, the order of the critical strain at which saturation occurs in J_e, and the ratio of the PEE intensity of deformed and undeformed crystals. At lower values of the strain, some of the excited electrons are captured by surface traps, where the deformation generated electric field is not able to cause the exo-emission. At larger deformation (in between 2% and 3%) of the crystal, the deformation-generated electric field becomes sufficient to cause an additional exo-electron emission of the electrons trapped in surface traps, and therefore, there appears a hump in the J_e versus ε curves of the crystals.

Keywords. Photo-stimulated exo-electron emission; alkalihalide crystals; plastic deformation; colour centres.

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1. Introduction

The optical excitation of electron coloured centres leads to electron emission. This phenomenon is known as photo-induced electron emission (PEE). The PEE is observed for absorption in the region of F-, K-, and L-bands of the F-centres. In any case, an extra thermal activation is required for the escape of electrons into the vacuum. The phenomenon of PEE in alkali halide crystals has been reviewed by Bichevin [1].

An additional stimulation increasing the flux of excited electrons towards the surface enhances the PEE intensity. It has been known for a long time that the role of such a stimulator can be played by plastic deformation of crystals. In 1984, Tsal et al [2] detected a sharp increase in the intensity of the PEE from γ-irradiated crystal of NaCl

excited with F-light under additional plastic deformation. The emission intensity increased by a factor of several times in comparison with the total intensities of the DEE and PEE under the combined action of deformation and irradition. This effect was subsequently studied by Poletaev and Shmurak [3] who referred to it as disloca- tion sensitized photostimulated exo-electron emission (DSPEE). Poletaev [4] and Poletaev and Shmurak [3] have investigated the spectral and kinetic features of DSPEE in additively coloured KCl crystals. Apart from the F-band, [5], they also studied the effect during the excitation of the K-, L_1- and L_2-bands. It was found that the plastic deformation barely changes the positions of the excitation bands while the integral intensity can increase by 15–30 times. Under the combined action of light in the region of the F-absorption band and deformation, the intensity of the DSPEE was 6–10 times greater than the intensity of DEE. At constant illumination the intensity of the DSPEE was non-monotonically dependent on the strain ε of the crystal. At small ε, a fall off in the emission intensity is observed, which can be understood in terms of the capture of excited electrons on the new traps which have arisen during deformation [6]. The emission intensity increases linearly with ε and when $\varepsilon \approx 2\%$, it attains a maximum, after which it falls off by 10–15% and when $\varepsilon \geq 3\%$, it remains constant up to the deformations which cause the sample to fracture. Similar behaviour in the intensity of the DSPEE was previously observed by Tsal and co-workers [2].

A field mechanism of DSPEE has been proposed by Molotskii and Shmurak [6]. Since the intensity of the DSPEE is 6–10 times greater than the intensity of DEE, the Auger process leading to DE were not taken into account in it. According to Molotskii and Shmurak [6], the increase in the intensity of the photoemission from F-centres during the plastic deformation is caused by the appearance of an electric field which draws excited electrons out of the deeper layers and thereby increases the number of electrons which reach the surface. Although the field emission theory of DSPEE proposed by Molotskii and Shmurak [6], is successful in explaining the linear increase of DSPEE intensity at low deformation, and the occurrence of saturation at higher values of the deformation, it has the following drawbacks:

(i) For $Y_S = 0.5$, $l_d \approx 10^{-4}$ cm, [6], the value of $[\Delta J_e(\varepsilon)/J_e(o)]$, varies from 5000 to 50, when the value of α_F varies from 1 to 100. This is nearly 20 to 30 times higher as compared to that of the experimentally observed values of $[\Delta J_e(\varepsilon)/J_e(o)]$ [2, 3, 6].

(ii) As g_0, α_F and l_d are independent of the electron affinity of the crystals, the equation derived by Molotskii and Shmurak (1990), shows that the intensity of PEE in non-deformed crystals, should be independent of the electron affinity. However, the intensity of DSPEE has been found to be correlated with the electron affinity of the crystals [3].

(iii) As $\alpha_F l_d \ll 1$, the equation derived by Molotskii and Shmurak [6] suggests that the temperature dependence of the PEE intensity of non-deformed crystals should be similar to that of l_d. This is not able to explain the temperature dependence of PEE intensity of the non-deformed crystals which follows the Arrhenius plot with an activation energy equal to the electron affinity i.e. $J_e(o) \propto \exp(-\chi/kT)$ [3].

The above drawbacks in the Molotskii's field emission theory of DSPEE indicate the need of a new theory. In the present paper we report a new field emission theory of DSPEE.

2. Theory

When a crystal surface is exposed to light of intensity I_d, then light absorption takes place within a certain depth of the crystal and the light intensely falls off exponentially with the distance x from the surface. Therefore, the rate of excitation of F-centres will be equal to $g_0 \exp(-\alpha_F x)$, where α_F is the absorption coefficient of the F-centre and x is the distance from the surface of the crystal. Thus, the rate of excitation of electrons from the F-centres may be given by

$$g_e = \frac{dn_e}{dt} = g_0 \exp(-\alpha_F x). \tag{1}$$

If p_{e1} is the rate constant for the jumping of excited electrons to the conduction band and p_{e2} is the rate constant for the dropping back of the excited electrons to the normal F-level, then we may write the following rate equation [7]

$$\frac{dn_e}{dt} = g_e - p_{e1} n_e - p_{e2} n_e.$$

Integrating the above equation and taking $n_e = 0$, at $t = 0$, we get

$$n = \frac{g_e}{(p_{e1} + p_{e2})} \{[1 - \exp -(p_{e1} + p_{e2})t]\}. \tag{2}$$

For $(p_{e1} + p_{e2})t \gg 1$, i.e. in equilibrium, we get

$$n_e = \frac{g_e}{(p_{e1} + p_{e2})} \tag{3}$$

Thus, the rate of generation of electrons in the conduction band may be written as

$$g_c = p_{e1} n_e = \frac{p_{e1} g_e}{(p_{e1} + p_{e2})}$$

or

$$g_c = \beta_1 g_0 \exp(-\alpha_F x), \tag{4}$$

where $\beta_1 = \frac{p_{e1}}{(p_{e1} + p_{e2})}$.

If τ_0 is the lifetime of the electrons in the conduction band of the crystal, then in equilibrium the number of electrons in the conduction band may be expressed as

$$(n_c)_{st} = \beta_1 \tau_0 g_0 [\exp(-\alpha_F x). \tag{5}$$

In the steady state, the number of conduction electrons lying in between x and $x + dx$, is given by

$$(dN_c)_{st} = n_c dx.$$

Therefore, the number of conduction electrons lying in between θ and x is given by

$$(N_c)_{st} = \int_0^x \beta_1 \tau_0 g_0 [\exp(-\alpha_F x)] dx \tag{6}$$

or

$$(N_c)_{st} = \frac{\beta_1}{\alpha_F} \tau_0 g_0 [-\exp(-\alpha_F x)]_\theta^x$$

or

$$(N_c)_{st} = \frac{\beta_1}{\alpha_F} \tau_0 g_0 [1 - \exp(-\alpha_F x)]. \tag{7}$$

From the above equation, the rate at which the conduction electrons are reaching within the distance θ to x, may be given by

$$R_c = \frac{(N_c)_{st}}{\tau_0}$$

or

$$R_c = \frac{\beta_1}{\alpha_F} g_0 [1 - \exp(-\alpha_F x)]. \tag{8}$$

When the crystal is deformed, an electrostatic field is produced on the surface of the crystal because of the movement of charged dislocations towards the surface and the strength of the field is given by [8, 6]

$$E_d = \frac{4\pi \varepsilon q}{K_0 b},$$

where q is the linear charge density of a dislocation, b is the Brugers vector, and K_0 is the dielectric constant of the crystal.

The drift length l_e is equal to $\mu_e E_d \tau_0$. Thus, we have

$$l_e = \frac{4\pi \varepsilon q}{K_0 b} \mu_e \tau_0. \tag{9}$$

Considering that the deformation induced electric field on the surface of the crystal is able to attract the conduction electrons lying within the distance θ to l_e, the intensity of DSPEE from equations (8) and (9) may be given by

$$J_e = \frac{Y_S \beta_1}{\alpha_F} g_0 \left[1 - \exp\left(-\frac{\alpha_F 4\pi \varepsilon q}{K_0 b} \mu_e \tau_0 \right) \right], \tag{10}$$

where Y_S is the fraction of the surface on which a positive charge arises during the deformation. For smaller value of the strain ε or for the smaller value of the field E_d, equation (10) may be written as

$$J_e(\varepsilon) = Y_S \beta_1 g_0 \frac{4\pi \varepsilon q}{K_0 b} \mu_e \tau_0. \tag{11}$$

The above equation shows that at low value of ε, the intensity of DSPEE will be proportional to the strain ε of the crystal. Such results have been obtained by Molotskii and Shmurak [6].

As the electric field intensity increases with the deformation, the depth of electron escape and thereby the flux of the emitted particles increases. However, when the escape depth l_e reaches a value such that $\alpha_F l_e \approx 1$, then saturation occurs since all the excited

electrons are extracted onto the crystal surface. Therefore, the critical deformation ε_c may be obtained by writing $l_e = 1/\alpha_F$, in eq. (9) and we get

$$\varepsilon_c = \frac{K_0 b}{4\pi q \mu_e \tau_0 \alpha_F}. \tag{12}$$

From equation (10), the saturation value of $J_e(\varepsilon)$ is given by

$$J_{es}(\varepsilon) = Y_s \frac{\beta_1 g_0}{\alpha_F}. \tag{13}$$

When the crystal will not be deformed, some of the electrons from the conduction band will reach the surface due to the diffusion process. As the rate of generation of excited electrons is equal to $g_0 \exp(-\alpha_F x)$, the rate of generation of electrons in the conduction band will be $\beta_1 g_0 [\exp(-\alpha_F x)]$. If χ is the electron affinity, then the probability of exo-emission of the electrons in the conduction band is, $P = \exp[-(\chi/kT)]$ [6]. Thus, the intensity of DSPEE in undeformed crystal is given by

$$J_e(0) = P\beta_1 g_0 [\exp(-\alpha_F x)]$$

or

$$J_e(0) = \beta_1 g_0 \left[\exp\left(\frac{\chi}{kT}\right) \right][\exp(-\alpha_F x)]. \tag{14}$$

In non-deformed crystal $\varepsilon = 0$, and thereby the electric field is absent. In this case, the depth of the layer from which excited electrons are capable to reach the surface will be equal to the diffusion length l_d. Thus, by taking $x = l_d$ in eq. (12), we get

$$J_e(0) = \beta_1 g_0 \left[\exp\left(-\frac{\chi}{kT}\right) \right][\exp(-\alpha_F l_d)]. \tag{15}$$

Since $\alpha_F l_d \ll 1$, the above equation may be written as

$$J_e(0) = \beta_1 g_0 \left[\exp\left(-\frac{\chi}{kT}\right) \right]. \tag{16}$$

From equations (13) and (16), we have

$$\frac{J_{es}(\varepsilon)}{J_e(0)} = \frac{Y_S}{\alpha_F} \exp(\chi/kT). \tag{17}$$

The above equation shows that the ratio of the saturation value of DSPEE intensity in deformed crystal to the DSPEE intensity in non-deformed crystal for the same intensity of light, will depend on α_F, χ and T.

The relative variation in the density of DSPEE is given by

$$\frac{\Delta J(\varepsilon)}{J(0)} = \frac{J(\varepsilon) - J(0)}{J(0)}$$

or

$$\frac{\Delta J(\varepsilon)}{\Delta J(0)} = \left[\frac{Y_S}{\alpha_F} \exp\left(\frac{\chi}{kT}\right) - 1 \right]. \tag{18}$$

3. Correlation between the theoretical and experimental results

Molotskii and Shmurak [6] have investigated the spectral dependence of PEE
for additively coloured KCl crystal by exciting the crystal to the K, L_1 and L_2
bands. It has been found that the plastic deformation has practically no influence
on the position of the exciting ion bands, while the integral intensity of the emission
increases 15–30 times (figure 1). The relationship between the band intensiy is
also changed. In deformed crystal, the main contribution to emission was made
by the L bands, and the contribution of the F and K bands is smaller. The deforma-
tion of the crystal increases the contribution of the F-band which grows nearly
5 times faster than the L bands. The intensity of all the bands increases, but non-
uniformly. For example, at strain $\varepsilon = 4 \times 10^{-5}$ s^{-1}, the contribution of the F-band
increases 28 times and that of the K and $L(L_1, L_2)$ band increases 20·9 times and 8·5
times, respectively.

It is seen from figure 2 that the DSPEE intensity depends non-monotonously on the
degree of deformation ε at a constant illumination. At low strain ε, the emission
intensity J_e falls which can be explained by capturing of electrons into the new traps
formed during the deformation. With increasing ε, the emission intensity grows rapidly
and at $\varepsilon \approx 2\%$, reaches its maximum, then J_e decreases by 10 to 15% and at $\varepsilon \simeq 3\%$
remain constant up to the deformation producing failure. This dependence is observed
for all excitation bands. For comparison the dependence of the DEE intensity on ε is
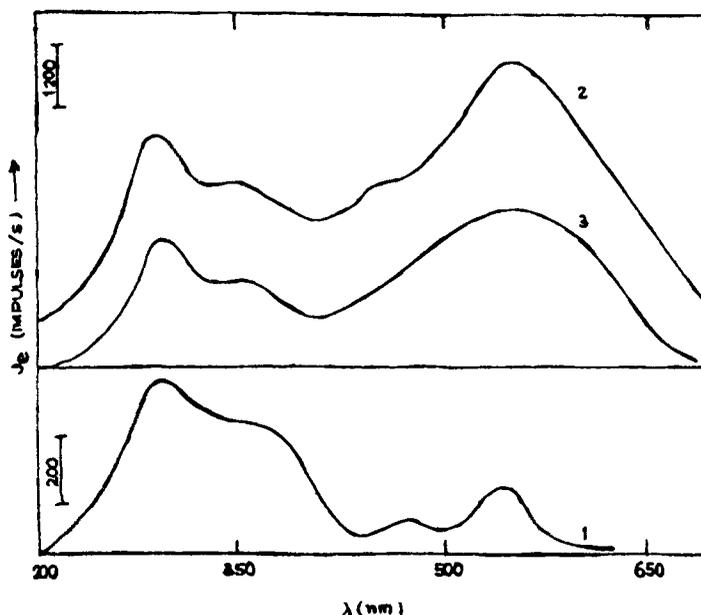also shown in figure 1 (Curve 4). It is seen that with the simultaneous action of the

Figure 1. Spectral dependence of photo-exo-emission (PEE) for additively
coloured KCl crystal. Curve 1–Initial spectrum, Curve 2 – PEE spectrum during
plastic deformation, Curve 3 – PEE spectrum on applying an external electric field
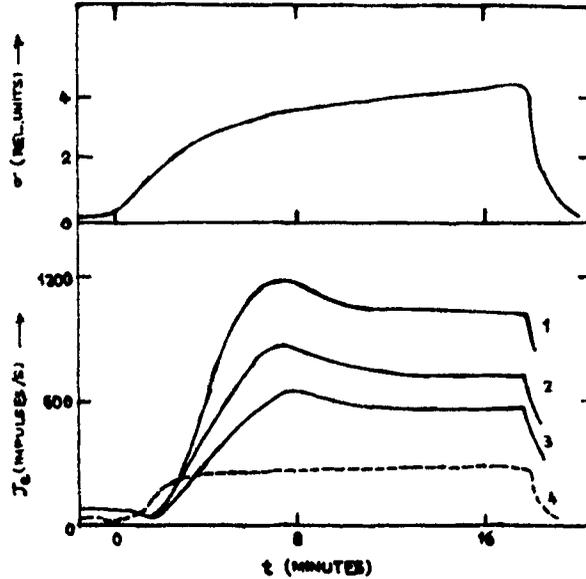of $E = 10^4$ V/cm [6].

Figure 2. Photo-exo-emission with plastic deformation of an additively KCl crystal. The upper curve is the deformation diagram. Curves 1, 2 and 3 have been obtained on illuminating the crystal with $\lambda_{max} = 560$ nm and 375 nm, respectively. Curve 4 is the dislocation exoemission of the strain rate $\varepsilon = 4 \times 10^{-5} S^{-1}$ [6].

deformation and illumination in the F-band, the DSPEE intensity is 6 to 10 times higher than that of DEE.

Equation (10) shows that for low value of ε, J_e should increase linearly with the strain ε. Such strain dependence of J_e can clearly be seen from figure 2. Equation (10) indicates that for large value of the strain ε, J_e should attain a saturation value. This fact is supported by the experimental results illustrated in figure 2.

Equation (15) shows that the PEE intensity in non-deformed crystal should follow the Arrhenius plot wih the activation energy χ. Poletaev and Shmurak [5] have measured the temperature dependence of PEE and they have found experimentally the temperature dependence similar to that suggested by equation (15). Using the temperature dependence of PEE intensity, they have succeeded in determining the value of electron affinity χ which is $0\cdot16 \pm 0\cdot2$ eV for KCl crystals.

Molotskii and Shmurak [6] have measured the dependence of PEE intensity on the externally applied electric field. They have found that PEE intensity increases linearly with the applied electric field (figure 3). This fact is in accord with the discussion made in our field emission theory of DSPEE (may be inferred from eq. (10)).

The theory proposed by us suggests that J_{es} and J_{e0} are correlated in the following way

$$\frac{J_{es}}{J_{e0}} = \frac{Y_S}{\alpha_F l_d}.$$

For KCl crystal in which most of DSPEE measurements have been made, $\chi = 0\cdot16$ eV and at $T = 300$ K, $\exp(\chi/kT)$ is equal to 470. The value of α_F in X- or
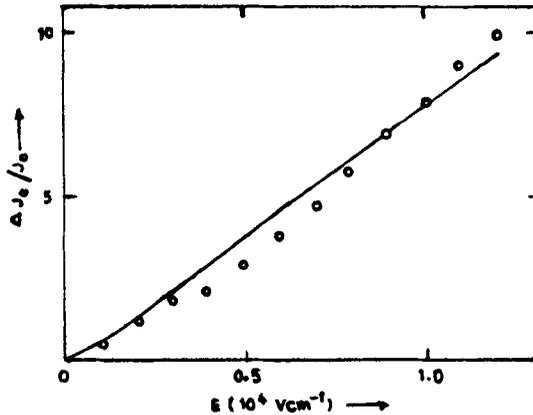
Figure 3. PEE intensity as a function of the electric field strength for additively coloured KCl crystal, 6 experimental data. Continuous curve is the calculated dependence of the PEE on the electric field strength $\Delta(J_e/J_p) = f(e)$ for $\mu_0 \tau_0 = 2 \cdot 2 \times 10^{-7} \text{cm}^2/\text{V}$ [6].

γ-radiated KCl crystal depends on the radiation doses given to the crystal and it varies from a lower value up to nearly 100. Thus, for $\alpha_F = 1$, J_{es}/J_{e0} will be 470, however, for $\alpha_F = 100$, J_{es}/J_{e0} may be 4·7. These results are in accord with the experimental observations [4–6].

For KCl crystals, $q = 5 \times 10^{-5}$ CGS/cm, $\mu_e = 6 \cdot 4 \text{cm}^2/\text{vs}$, $K_0 = 6$, $b = 4 \cdot 44 \text{Å}$, $\alpha_F = 25 \text{cm}^{-1}$, and $\tau_0 \approx 2 \times 10^{-7}$ s. Thus, the critical value of strain ε at which saturation value in DSPEE will occur, comes out to be $\varepsilon_c \approx 2\%$ (equation 9). Experimentally DSPEE intensity is found to attain a saturation value nearly at $\varepsilon \approx 2\%$. This finding also supports the correlation between the theoretical and experimental results.

It is seen from figure 2 that there is a hump at a strain in between 2% and 3%. It seems that at lower values of the strain, some of the excited electrons are captured by surface traps, where the deformation generated electric field is not able to cause the emission of these surface trapped electrons. At larger deformation the deformation generated electric field becomes sufficient to cause the additional exo-emission of the electrons trapped in surface traps. As a matter of fact, a hump appears in the J_e versus ε curves of the crystals.

4. Conclusions

A new field emission theory of DSPEE is explored which is able to explain several experimental observations like linear increase of DSPEE intensity J_e with the strain at low deformation, occurrence of the saturation in J_e at higher deformation, temperature dependence of J_e, linear dependence of J_e on the electric field strength, the order of the critical strain at which saturation occurs in J_e, and the ratio of the PEE intensity of deformed and non-deformed crystals. The change over by which the excited electrons emerge onto the surface from a diffusion mechanism to a drift mechanism enables one to account for the observed pronounced growth in the intensity of the

photo-stimulated emission of F-centre electrons during the plastic deformation of alkali halide crystals.

At lower values of the strain, some of the excited electrons are captured by surface traps, where the deformation generated electric field is not able to cause the exo-emission. At larger deformation (in between 2% and 3%) of the crystal, the deformation generated electric field becomes sufficient to cause the additional exo-electron emission of the electrons trapped in surface traps. Therefore, there appears a hump in the J_e versus ε curves of the crystals.

A good correlation between the theoretical and experimental results indicates that the DSPEE is primarily due to the electric field developed on the surface of the crystal during the process of their mechanical deformation.

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